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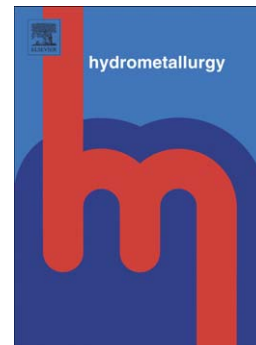
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## Novel lead-cobalt composite anodes for copper electrowinning

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### *Abstract*

PbO<sub>2</sub>-CoO<sub>x</sub> and PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> composite coated anodes, using titanium and nickel substrates, have been successfully prepared and tested under typical copper electrowinning conditions. The aim of depositing a well-adhered composite coating onto the surface of the titanium and nickel substrate materials was pursued using three different coatings. The performance of the produced anodes was examined in terms of oxygen evolution potential and service life. Both of the anodes with PbO<sub>2</sub>-CoO<sub>x</sub> or PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> deposited on titanium resulted in reduction of the oxygen evolution potential of 300 to 400 mV compared with a conventional PbCaSn anode. The anodes prepared by applying the same coatings onto a nickel substrate showed poor stability in the acidic electrolyte media used in this experiment to represent typical copper electrowinning conditions. Of the different coatings tested, a combination of thermal deposition of a SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> interlayer on the surface of a titanium substrate followed by electrodeposition of the top layer of the composite coating resulted in the best electrochemical activity and service life for the anodes. A Tafel slope of 88 mV dec<sup>-1</sup> was recorded for the anode with a top coating of PbO<sub>2</sub>-CoO<sub>x</sub> and 47 mV dec<sup>-1</sup> for the anode with a top coating of PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>, which both compare favourably to the 122 mV dec<sup>-1</sup> which was observed for a conventional PbCaSn anode. Anodisation tests were carried out for a period of 16 hours both in the presence and in the absence of the organic additive thiourea in the electrolyte. Corrosion rates were estimated from these tests and the results showed that the titanium based anode with a SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> interlayer and PbO<sub>2</sub>-CoO<sub>x</sub> coating has a lower corrosion rate than a conventional PbCaSn anode, whereas the corrosion rate of the titanium based anode with same interlayer and PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> coating might be much greater but this remains to be confirmed. The results also showed that the addition of thiourea appears to increase the corrosion rate of the composite coated anodes although it reduces the corrosion rate of a PbCaSn anode. Thiourea showed no obvious effect on the anode potential.

*Keywords: Composite anode, Electrowinning, Lead, Cobalt, Titanium*

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## 1 INTRODUCTION

In coated anodes containing a  $\text{PbO}_2$  layer deposited on top of an inert substrate, titanium is the most widely used substrate (Gonzalez-Garcia et al., 1999) due to its corrosion resistance (Pouilleau et al., 1997). Generally, substrates are chosen for good mechanical and chemical stability and are frequently pre-treated to clean the surface before coating, either by polishing, chemical or electrochemical methods (Bard et al., 2001). In the case of lead-titanium anodes, titanium usually stabilizes the lead, preventing it from spalling and passivation (Weems and Schledorn, 2005). Beer (1966) in the 1960s proposed that titanium can be used as a substrate in industrial applications to produce dimensionally stable anodes (DSAs). Such anodes are usually used in the evolution of chlorine or oxygen (Devilliers et al., 2004). Titanium's resistance to corrosion is due to the formation of a very stable passive  $\text{TiO}_2$  layer on the surface of the metal. However, the gradual thickening of this oxide layer can also lead to deactivation of the DSA anodes. The method in which the anode coating is applied and how the substrate is prepared, determine the subsequent stability and electrochemical properties of the coated anode. The most widely investigated Ti-based anode for oxygen evolution has an iridium dioxide coating. The service life of this anode is reported to be around 20 times longer than another common type of anode which has a ruthenium dioxide coating (Alves et al., 1998). On the other hand,  $\text{IrO}_2$  is more expensive than  $\text{RuO}_2$  and its electrocatalytic activity is slightly lower (Chen et al., 2001). As anodes with a lead dioxide coating possess high electrical conductivity, good electrochemical and chemical stability against corrosion and are relatively inexpensive, researchers have long considered using lead dioxide as a surface layer on a Ti substrate, with the lead dioxide sometimes doped with other metal oxides such as  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{CoO}_x$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{RuO}_2$  and others (Velichenko et al., 2009a, 2009b and 2009c; Yeo et al., 2010; Morimitsu et al., 2010; Cattarin et al., 2001; Musiani et al., 1997; Bertoncello et al., 2000).

The present paper contributes to this field of study by focusing on the preparation and performance characterisation of lead dioxide coatings incorporating cobalt oxides, deposited onto either titanium or nickel substrates. It is well established in electrowinning applications that cobalt, added into the electrolyte, or added as an alloying element or on the surface layer of an anode, reduces the operating potential and corrosion rate of lead based anodes, while the lower lead dioxide formation contributed to the quality of the produced cathodes (Bagshaw, 1997; Cachet et al., 1999; Hrussanova et al., 2001, 2004a, 2004b; Rashkov et al., 1999; Yu and O'Keefe 1999). A literature review on the influence of cobalt in the electrolyte solution on the performance of lead based anodes in copper electrowinning was provided by Nikoloski and Nicol (2008), followed by a separate review focusing on the direct addition of cobalt to the lead surface layer (Nikoloski and Nicol, 2010). These papers outline the

effects of cobalt addition, either to the electrolyte or to the surface layer of the anode, and show that in both cases the main benefits involve i) reduced energy consumption due to a lower operating potential for the anodes and ii) reduced anode corrosion resulting in less of the corrosion product  $\text{PbO}_2$  being produced and migrating through the electrolyte to contaminate the cathode. Therefore, effective doping of  $\text{PbO}_2$  with cobalt oxides potentially constitutes another option for a stable coating suitable for use on an anode in acidic media.  $\text{PbO}_2\text{-CoO}_x$  and  $\text{PbO}_2\text{-Co}_3\text{O}_4$  coated anodes have been reported to perform well in basic media and in water electrolysis systems (Musiani and Guerriero, 1998, Musiani et al., 1999). However, to our knowledge, there is no information about the performance of  $\text{PbO}_2\text{-CoO}_x$  and  $\text{PbO}_2\text{-Co}_3\text{O}_4$  coated anodes in acidic media in the literature. To investigate these coatings,  $\text{PbO}_2\text{-CoO}_x$  and  $\text{PbO}_2\text{-Co}_3\text{O}_4$  coated anodes, with and without an interlayer, were prepared using both titanium and nickel substrates with the aim of producing stable composite anodes that can operate with low oxygen evolution potential and have long service life under conditions typically encountered in copper electrowinning.

## 2 EXPERIMENTAL METHODS AND MATERIALS

Preparation of the coated anodes was carried out using a standard three-electrode electrochemical system. The reference electrode was a mercury mercurous sulphate electrode (MSE). All potentials are reported in the normal hydrogen electrode (NHE) scale. The ohmic drop between the reference and working electrode was not compensated. In every experiment, a fresh substrate was used, with an exposed surface to the electrolyte of  $19.62 \text{ mm}^2$ . The substrate material for the coated titanium electrodes was titanium grade 2 rod supplied by Titanium International. The substrate material for the coated nickel electrodes was nickel rod with 99.99 % purity supplied by Good Fellows. A glass cell with a plastic lid was used to hold the anode, the cathode and the reference electrode. The temperature was kept constant during the experiments by using a thermostated water bath. The generated data was recorded on a computer using LabVIEW<sup>®</sup> 7.1 software. Potentiostat EG&G Princeton Applied Research, model 173, was used in all experiments.

### 2.1 Preparation of composite coated anodes

Six different composite coatings were prepared and tested in this study: (a) three coatings with  $\text{PbO}_2\text{-CoO}_x$  as the surface layer; and (b) three coatings with  $\text{PbO}_2\text{-Co}_3\text{O}_4$  as the surface layer. The three different coating types were produced as follows:

- A. Direct anodic deposition of a lead-cobalt composite coating onto the surface of the substrate.
- B. Electrodeposition of a metallic Pb interlayer prior to anodic deposition of a composite layer.

C. Thermal deposition of an  $\text{SnO}_2\text{-Sb}_2\text{O}_3$  interlayer prior to anodic deposition of a composite layer.

### 2.1.1 Pre-treatment of substrates

In each experiment, the substrates were subjected to pre-treatment to clean the surface and ensure uniform coverage by the coatings over the entire surface area. The pre-treatment of substrates consisted of several steps, involving wet polishing the substrate with successively finer (600 and 1200 grit) SiC papers, followed by 10 minutes of cleaning in an ultrasonic bath containing DI water. In the case of the Ti substrate, the Ti was then subjected to an etching procedure of boiling in 10% oxalic acid for 2 h. Next, substrates were rinsed with deionised (DI) water and dried in a stream of air.

### 2.1.2 $\text{PbO}_2\text{-CoO}_x$ composite coatings

$\text{PbO}_2\text{-CoO}_x$  coating was anodically electrodeposited from an electrolyte containing lead and cobalt ions prepared by adding 0.5 M lead sulphamate and 0.5 M cobalt nitrate salt. The pH of the electrolyte was adjusted to 1.6. The electrodeposition was performed potentiostatically at 1.75 V at 25°C for 2 h. This produced **coating type A**. To produce **coating type B**, a metallic Pb interlayer was cathodically deposited onto the substrate by potentiostatic polarisation at -0.625 V from the above mentioned electrolyte for 1 h. The composite  $\text{PbO}_2\text{-CoO}_x$  coating was then anodically deposited by polarising the electrode at 1.6 V. To produce **coating type C**, a  $\text{SnO}_2\text{-Sb}_2\text{O}_3$  interlayer was thermally deposited onto the substrate prior to the anodic deposition of  $\text{PbO}_2\text{-CoO}_x$ . To apply the  $\text{SnO}_2\text{-Sb}_2\text{O}_3$  interlayer, a precursor solution was prepared by dissolving 20 g  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , 2 g  $\text{SbCl}_3$  and 13.2 mL HCl into 100 mL of isopropanol. The pre-treated substrate was dipped in the precursor solution for 5 minutes followed by 15 minutes of drying in an oven at 110°C. This procedure was repeated 3 times. The anode was then annealed in a muffle furnace at 500°C for 1 h. Fresh precursor solution was used for each treatment. A  $\text{PbO}_2\text{-CoO}_x$  composite layer was electrodeposited from the same electrolyte containing lead and cobalt described above. The electrodeposition was carried out potentiostatically at 1.75 V over a period of 2 h.

Table 1 summarises the coating composition of the different  $\text{PbO}_2\text{-CoO}_x$  composite anodes used in this study.

*Table 1. Composition of  $\text{PbO}_2\text{-CoO}_x$  composite coated anodes without an interlayer and with different interlayers*

### 2.1.3 PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> composite coatings

The method of anodic electrodeposition of the PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> composite coatings used in this study involved preparing a bath containing lead ions and suspended Co<sub>3</sub>O<sub>4</sub> particles. The coating electrolyte was made up with 0.13 M lead acetate and 0.9 M lead nitrate salt and combined with 5% w/v of Co<sub>3</sub>O<sub>4</sub> (powder < 10 µ) supplied by Sigma Aldrich. The solid particles were kept in suspension by mild agitation. The pH of the electrolyte was adjusted to 4.4. The temperature of the bath was maintained at 25°C and the electrodeposition was carried out potentiostatically at 1.75 V for 2 h. This technique when applied directly using either titanium or a nickel rod produced **coating type A**. To produce **coating type C**, the deposition technique for a SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> interlayer described in 2.1.2 was used, followed by electrodeposition of PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> composite coating as described above. For this composite coating, electrodes with Pb interlayer (**coating type B**) were not produced because of inadequate protection from this interlayer observed in the tests involving the PbO<sub>2</sub>-CoO<sub>x</sub> composite coatings. In each case, immediately after the preparation of the coating, the composite coated anode was rinsed with DI water and dried in air under ambient conditions. Details of the composition of the different PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> composite coatings are summarised in Table 2.

*Table 2. Composition of PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> composite coated anodes without an interlayer and with different interlayers*

## 2.2 Physical characterisation

The surface of the composite coated anodes was observed using a scanning electron microscope (SEM) model Philip XL20, which was equipped with an energy dispersive X-ray spectroscopy (EDS) Oxford Link ISIS model 5175. This method was also used to determine the surface composition of the different composite coated anodes.

## 2.3 Electrochemical characterisation

### 2.3.1 Anodisation tests

Short term (16 h) and long term (168 h) anodisation tests were conducted to evaluate the anode potential of each composite coated anode under typical copper electrowinning conditions. The composite coated anodes were tested by anodisation in an electrolyte containing 180 g dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> prepared using Analytical Reagent (AR) grade sulphuric acid in DI water, by conducting

galvanostatic polarisation at a current density of  $300 \text{ A m}^{-2}$ . The temperature of the electrolyte was maintained at  $40 \pm 2 \text{ }^{\circ}\text{C}$  by circulating water from a thermostated water bath and the electrolyte was agitated by a magnetic stirrer. During the anodisation, electrolyte solution samples were taken periodically to determine the amount of cobalt released to the electrolyte. The samples were analysed by Atomic Absorption Spectrophotometer (AAS) model GBC 933 PLUS. This was one indication of service life, as the amount of Co in the anode is critical to the effectiveness of the anode for copper electrowinning.

### 2.3.2 Cyclic Voltammetry

Cyclic voltammetry was used to estimate the starting potential for oxygen evolution on the fresh composite coated anodes in  $180 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4$  and compare this with the oxygen evolution potential on a conventional (uncoated) PbCaSn anode. Overpotential for the start of the oxygen evolution reaction was thus estimated as the difference between the observed potential for oxygen evolution during the anodic polarisation scan and the standard potential calculated for the system, which under the conditions involving  $180 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4$  and  $40 \text{ }^{\circ}\text{C}$  is  $1.236 \text{ V}$ . The potential of the working electrode (anode) was cycled from the initial potential, which was the rest potential observed on a freshly prepared composite coated anode during open circuit potential measurement, to  $+2 \text{ V}$  and then swept back to  $-1 \text{ V}$  at a scan rate of  $2 \text{ mV sec}^{-1}$ . Overpotential for oxygen evolution was also determined during steady operation at  $300 \text{ A m}^{-2}$ , on both the fresh anode surface and after a 16 h period of conditioning. These measurements were taken from potential-time transients recorded at the start and end of each test.

In addition, using cyclic voltammograms the corrosion rates of the composite coated anodes were estimated over 16 hours of operation. The corrosion rate was calculated from the area under the  $\text{PbO}_2\text{-PbSO}_4$  reduction peak. These measurements were also done in the presence of  $10 \text{ mg dm}^{-3}$  thiourea in the electrolyte, as thiourea has been observed to reduce corrosion rates for lead anodes (Barmi and Nikoloski, 2012; Ehsani et al., 2012).

### 2.3.3 Tafel plot measurements

Tafel slopes of the anodic reaction were also measured to examine the electrochemical reaction rate characteristics on the different anodes. The data for the Tafel plots were generated from the same set of result recorded during the cyclic polarisation measurements, which the anodic Tafel slope for each anode estimated from the linear section of the log current density versus potential where the oxygen evolution reaction was observed to be activation controlled, which varied from one anode to another.



### 3 RESULTS AND DISCUSSION

#### 3.1 PbO<sub>2</sub>-CoO<sub>x</sub> composite coated anodes

A recent study (Barmi and Nikoloski, 2012) on the behaviour of Pb-Co and Pb-Co<sub>3</sub>O<sub>4</sub> composite coated anodes showed that incorporation of cobalt into the surface layer of the anode significantly reduces the anode potential as well as its corrosion rate. The present study evaluates the performance of composite lead dioxide coatings incorporating cobalt oxides, deposited either directly or with an interlayer onto titanium and nickel substrates. Figure 1 shows SEM images of fresh PbO<sub>2</sub>-CoO<sub>x</sub> coated anodes with different coating types and deposited onto either nickel or titanium substrates.

*Figure 1. SEM images of PbO<sub>2</sub>-CoO<sub>x</sub> composite coatings  
(A: Ni-PbO<sub>2</sub>-CoO<sub>x</sub>, B: Ti-PbO<sub>2</sub>-CoO<sub>x</sub>, C: Ti-Pb-PbO<sub>2</sub>-CoO<sub>x</sub>, D: Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-CoO<sub>x</sub> and E: Ni-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-CoO<sub>x</sub>)*

It is apparent that the surface structure of the Ni-PbO<sub>2</sub>-CoO<sub>x</sub> anode (Figure 1-A) was brittle and cracked. The results of anodisation of this composite coated anode in 180 g dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> showed that it was not able to cope with the stresses from anodisation.

The same coating electrodeposited under the same conditions onto the titanium substrate (Figure 1-B) showed a similar cracked surface structure. This anode also did not perform well under the anodisation test conditions. In the early stages of anodising the Ti-PbO<sub>2</sub>-CoO<sub>x</sub> coated anode, detachment of the surface layer was observed. Detachment of part or the entire surface layer leaves the Ti substrate in contact with the acid electrolyte and allows a non-conductive TiO<sub>2</sub> layer to grow and dramatically increase the anode potential. Poor cleaning and insufficient or incorrect pre-treatment can be two of the main reasons for detachment of a composite layer from the substrate. Localised lifting of the coating can then cause failure of the composite layer (Kanani, 2004). Although this Ti based composite coated anode showed high electrocatalytic activity (reduction of overpotential for the oxygen evolution reaction) it degraded within 30 minutes of the start of the anodisation test.

An essential criterion for use of an anode in copper electrowinning is adequate service life. Hence, in order to prevent the growth of TiO<sub>2</sub> on the surface of the titanium substrate and thereby improve the stability of the coated anode, a lead interlayer (Yeo et al., 2010) was added to the anode structure in

Figure 1-B, resulting in an anode with surface structure shown in Figure 1-C. This coating appeared denser than the coating without an interlayer, but cracks were still present. Initially, the oxygen evolution reaction was somewhat depolarised on the surface of this composite coated anode, probably due to seemingly increased surface area, but it was short lived. The surface coating was not stable and flaked off during anodisation testing, and this appeared to be the main reason for the observed degradation of the performance during testing. The removal of part or all of the coating places titanium in a direct contact with the electrolyte leading to passivation through formation of  $\text{TiO}_2$ , which was evidenced by the ascending anode potential. As a result of the poor performance of this sample, this coating type with nickel substrate was not tested.

As an alternative to a lead interlayer, a  $\text{SnO}_2\text{-Sb}_2\text{O}_3$  interlayer (Yang et al., 2009) was thermally deposited onto titanium prior to deposition of the  $\text{PbO}_2\text{-CoO}_x$  composite coating. This was also done using nickel as the substrate. Figures 1-D (Ti) and 1-E (Ni) show SEM images of the two freshly prepared composite coated anodes produced in this way. The application of a  $\text{SnO}_2\text{-Sb}_2\text{O}_3$  interlayer significantly improved the service life of the  $\text{Ti-SnO}_2\text{-Sb}_2\text{O}_3\text{-PbO}_2\text{-CoO}_x$  anode in the anodisation test. However, there was no obvious improvement of the  $\text{Ni-SnO}_2\text{-Sb}_2\text{O}_3\text{-PbO}_2\text{-CoO}_x$  anode compared to previously tested Ni-based anodes, and this anode degraded shortly after the application of current. Hence the  $\text{Ni-SnO}_2\text{-Sb}_2\text{O}_3\text{-PbO}_2\text{-CoO}_x$  anode was not further tested or analysed.

The titanium based composite coated anode in Figure 1-D initially contained 5.4 at.% Co incorporated into the surface layer, and showed enhanced stability and lower oxygen evolution potential for a period of 16 hours. During this time however, a gradual increase of the potential was observed, which could be attributed to the slow disbanding of the active sites which causes a reduced surface fraction of  $\text{CoO}_x$  (Musiani et al., 1999). EDS data for this composite coated anode after 16 hours of anodisation detected almost no cobalt on the surface, which confirms that the active surface layer was slowly dispersing with time. However, the  $\text{Ti-SnO}_2\text{-Sb}_2\text{O}_3\text{-PbO}_2\text{-CoO}_x$  anode demonstrated better stability than the other  $\text{PbO}_2\text{-CoO}_x$  coated anodes. Therefore, the further testing on a  $\text{PbO}_2\text{-CoO}_x$  coated anode was carried out just using this type of composite coated anode.

The next tests carried out involved cyclic voltammetry to estimate the overpotential for the start of the oxygen evolution reaction and compare this with the potential on a conventional  $\text{PbCaSn}$  anode surface. Figure 2 shows a cyclic voltammogram of the  $\text{Ti-SnO}_2\text{-Sb}_2\text{O}_3\text{-PbO}_2\text{-CoO}_x$  coated anode in  $180 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4$ . Scanning in the anodic direction, a sharp increase was observed at about 1.67 V which can be related to the simultaneous nucleation of  $\text{PbO}_2$  and evolution of oxygen. The

overpotential for the start of the oxygen evolution ( $\sim 440$  mV) is significantly lower on the surface of this composite coated anode than on a conventional PbCaSn anode surface, which was observed at overpotential of approximately 640 mV. In the return sweep, reduction of  $\text{PbO}_2$  to  $\text{PbSO}_4$  takes place at about 1.5 V. There is an insignificant peak at potential more negative than -0.3 V, which is linked to discharge of  $\text{PbO}_2$  and  $\text{PbSO}_4$  to Pb. The composite coated anode was virtually passive between 1.5 V to -0.3 V.

*Figure 2. Cyclic voltammogram of  $\text{Ti-SnO}_2\text{-Sb}_2\text{O}_3\text{-PbO}_2\text{-CoO}_x$  coated anode in  $180 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4$*

*Figure 3. Potential-time transients of  $\text{Ti-SnO}_2\text{-Sb}_2\text{O}_3\text{-PbO}_2\text{-CoO}_x$  and PbCaSn anode*

The  $\text{Ti-SnO}_2\text{-Sb}_2\text{O}_3\text{-PbO}_2\text{-CoO}_x$  coated anode operated initially at an anode potential more than 300 mV lower than that observed with the conventional PbCaSn anode. However, as is apparent from Figure 3, this difference in potential decreased after 15 minutes of polarisation to approximately 180 mV, and thereafter the potential of this composite coated anode gradually increased further over 16 hours of anodisation until its operating potential eventually become stable at 2.1 V, which is slightly higher although still relatively close to the stable anode potential observed for the conventional PbCaSn anode.

### 3.2 $\text{PbO}_2\text{-Co}_3\text{O}_4$ composite coated anodes

The composite coated anodes produced by direct deposition of  $\text{PbO}_2\text{-Co}_3\text{O}_4$  onto a nickel substrate and onto a titanium substrate showed relatively high and similar incorporation of cobalt into the composite layer ( $X_{\text{Co}} = 0.61$  and 0.60). However, these coatings were both unstable in the acid electrolyte during anodisation testing and were not subjected to further experiments.

The tendency of titanium to produce a nonconductive  $\text{TiO}_2$  layer, and its resistance to corrosion, are well known. By introducing an active metal/metal oxide composite layer on the surface, it is possible to combine the dimensional stability advantage of the titanium relative to lead with the oxygen evolution activity of the low cost lead-cobalt oxide compounds. Figure 4 shows SEM images of the surface of the composite coated anodes produced with a  $\text{SnO}_2\text{-Sb}_2\text{O}_3$  interlayer.

*Figure 4. SEM images of A: Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> and B: Ni-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> composite coatings*

Comparing Figure 4 and Figure 1 shows that the composite coatings produced using cobalt oxide particles have a much rougher surface than the coatings produced using cobalt nitrate solution leading to a large effective surface area. This has been reported previously by Velichenko et al. working with electrolytes containing suspended ZrO<sub>2</sub> grains (2008). High surface area is a favourable feature for anodes as it decreases the effective current density and therefore the operating potential of the anode. Musiani et al. (1997) observed the same phenomenon of decreased operating potential and related it to the incorporated Co<sub>3</sub>O<sub>4</sub> particles. They argued that Co<sub>3</sub>O<sub>4</sub> particles act as preferred sites for oxygen evolution.

Although the Ni-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> anode was dramatically enriched with cobalt (20 at. %), it underwent rapid degradation during the anodisation tests in the sulphuric acid electrolyte. Moreover, it was observed that the Ni-based coated anodes in all tests and regardless of the nature of composite layer used, corroded rapidly under anodic polarisation in the acid media. Addition of the organic additive thiourea was investigated as a potential remedy but it led to no improvement. From the conducted tests it is not possible to tell whether there was an improved catalytic effect for the oxygen evolution reaction caused by the presence of Co<sub>3</sub>O<sub>4</sub> in this coated anode. For the remainder of this section, the focus is therefore on the Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> anode.

The Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> anode contained about 3 at. % cobalt. A freshly prepared composite coated anode of this type was used for voltammetric measurements to assess its anodic properties. Figure 5 shows a single scan cyclic voltammogram using the Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> coated anode in 180 g dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>. Scanning in the anodic direction, a sharp increase was observed at about 1.56 V which can be related to the simultaneous nucleation of PbO<sub>2</sub> and evolution of oxygen. The overpotential for the start of the oxygen evolution reaction (~ 330 mV) is again significantly lower on the surface of this composite coated anode than on a conventional PbCaSn anode (~ 640 mV). In the return sweep, reduction of PbO<sub>2</sub> to PbSO<sub>4</sub> takes place at about 1.4 V. There is an insignificant peak at potential more negative than -0.3 V, which is attributed to discharge of PbO<sub>2</sub> and PbSO<sub>4</sub> to Pb.

*Figure 5. Cyclic voltammogram of Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> anode in 180 g dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>*

Figure 6 and 7 show that the Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> coated anode had very good stability and maintained a relatively stable anode potential of 1.73 V over 16 and 168 hours of polarisation.

The amount of cobalt released from the Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> anode surface to the electrolyte was monitored over a period of 168 hours of polarisation. It was observed that the release of cobalt from the anode is insignificant during the first 50 h (Figure 7). In the presence of 10 mg dm<sup>-3</sup> thiourea, a greater amount of cobalt was released initially but the concentration become stable after 100 hours. This composite coated anode showed significant depolarisation compared to the PbCaSn and great stability compared to the other coated anodes tested during the 168 hours of anodisation in the sulfuric acid electrolyte.

*Figure 6. Potential-time plot of Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> anode compared with a conventional PbCaSn anode*

*Figure 7. Release of cobalt from the composite coated anodes during anodic polarisation*

The Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> coated anode operated at an anode potential initially about 400 mV lower than that observed for the conventional PbCaSn anode. As the results in Figure 6 show, the operating potential of the Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> coated anode stabilises relatively quickly attaining a steady potential of 1.70 V after 10 minutes. This compares favourably to the PbCaSn anode which stabilises at 2.07 V after 20 minutes. Although the difference in potential between the two anodes gradually decreases with time to approximately 380 mV, partly due to the slow depolarisation of the PbCaSn anode, after 16 hours of anodisation the composite coated anode is still operating at a potential of 1.73 V, which is a significant improvement compared to the conventional PbCaSn anode.

### 3.3 Corrosion rates

The corrosion rates of the two composite coated anodes with the most promising stability and operating characteristics, Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-CoO<sub>x</sub> and Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>, were estimated using cyclic voltammetry. Cathodic polarisation sweep measurements were conducted immediately after galvanostatic oxidation for a period of 16 h in 180 g dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>. Tests were

conducted both in the presence and absence of  $10 \text{ mg dm}^{-3}$  thiourea. The polarisation scans were performed at  $2 \text{ mV Sec}^{-1}$ , starting from the operating potential of the composite coated anode to  $-1 \text{ V}$ . The results are shown in Figures 8 and 9.

*Figure 8. Reduction sweep of  $\text{Ti-SnO}_2\text{-Sb}_2\text{O}_3\text{-PbO}_2\text{-CoO}_x$  anode after 16 h operation in the presence and absence of thiourea*

*Figure 9. Reduction sweep of  $\text{Ti-SnO}_2\text{-Sb}_2\text{O}_3\text{-PbO}_2\text{-Co}_3\text{O}_4$  anode after 16 h operation in the presence and absence of thiourea*

Comparing the cathodic peaks with and without thiourea in the electrolyte related to the reduction of  $\text{PbO}_2$  to  $\text{PbSO}_4$  reveals that in the presence of thiourea, the cathodic peaks are slightly larger. Therefore, higher corrosion rates might be expected for both  $\text{Ti-SnO}_2\text{-Sb}_2\text{O}_3\text{-PbO}_2\text{-CoO}_x$  and  $\text{Ti-SnO}_2\text{-Sb}_2\text{O}_3\text{-PbO}_2\text{-Co}_3\text{O}_4$  anodes in the presence of  $10 \text{ mg dm}^{-3}$  thiourea. The results also reveal that thiourea affects the behaviour of the  $\text{Ti-SnO}_2\text{-Sb}_2\text{O}_3\text{-PbO}_2\text{-CoO}_x$  anode much less than it affects the  $\text{Ti-SnO}_2\text{-Sb}_2\text{O}_3\text{-PbO}_2\text{-Co}_3\text{O}_4$  anode.

Table 3 shows the estimated corrosion rates obtained from reduction charge for a  $\text{PbCaSn}$  anode and for the two composite coated anodes. Information on the corrosion of  $\text{PbCaSn}$  anode operated in an electrolyte containing cobalt ions has been published recently (Barmi and Nikoloski, 2012).

*Table 3. Corrosion rates of composite coated anodes and  $\text{PbCaSn}$  anode in  $180 \text{ g dm}^{-3} \text{H}_2\text{SO}_4$*

The  $\text{Ti-SnO}_2\text{-Sb}_2\text{O}_3\text{-PbO}_2\text{-Co}_3\text{O}_4$  coated anode showed significantly higher corrosion rates than the  $\text{PbCaSn}$  anode both in the absence and presence of thiourea. However, this effect was more pronounced in the presence of thiourea, where the estimated corrosion rate of the composite coated anode was  $79 \text{ g kA}^{-1} \text{ h}^{-1}$ . It should be noted that this result might be influenced by the reduction of the cobalt oxide species present in the surface content. Further tests are being done to confirm this corrosion result.

The  $\text{Ti-SnO}_2\text{-Sb}_2\text{O}_3\text{-PbO}_2\text{-CoO}_x$  anode showed lower corrosion rates than the  $\text{PbCaSn}$  anode both in the absence and presence of thiourea. The introduction of thiourea still increased the corrosion rate of

the Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>- PbO<sub>2</sub>-CoO<sub>x</sub> anode, but by a small amount from 1.1 g kA<sup>-1</sup> h<sup>-1</sup> in the absence of thiourea to 1.3 g kA<sup>-1</sup> h<sup>-1</sup> in its presence. Hence thiourea appears to produce an increase in the formation of PbO<sub>2</sub> for both of the composite coated anodes. However, this finding is only for a single concentration (10 mg dm<sup>-3</sup>) of thiourea, and further tests with different concentrations of thiourea would need to be carried out to gain a better understanding of this effect. As thiourea leads to a reduction in corrosion rate for PbCaSn anodes, it may be that this finding is an indication of a different mechanism for the electrochemical reactions taking place in these lead oxide coated anode systems compared to a conventional PbCaSn anode.

### 3.4 Tafel plots

The overpotentials for the oxygen evolution reaction at the operating current density and the Tafel slopes for each of the titanium based composite coated anodes and PbCaSn are summarised in Table 4. All of the fresh composite coated anodes showed lower oxygen evolution overpotentials than a conventional PbCaSn anode (864 mV). However, there was variation in the surface roughness between the different anodes and only the two with a SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> interlayer also showed promising stability over 16 hours of anodisation. Another indicator of electrochemical reaction mechanisms is the Tafel slope under activation controlled conditions.

*Table 4. Overpotential for oxygen evolution reaction on the composite coated anodes*

The Tafel plot for oxygen evolution reaction on the Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-CoO<sub>x</sub> anode showed a slope of 88 mV dec<sup>-1</sup>, which is a distinct drop from the slope of 122 mV dec<sup>-1</sup> observed for a conventional PbCaSn anode but is similar to the slopes observed previously using lead based composite coated anodes with coatings containing lead and cobalt oxides (Barmi and Nikoloski, 2012). In addition, incorporation of Co<sub>3</sub>O<sub>4</sub> particles into the coating rather than CoO<sub>x</sub>, further reduced the Tafel slope to 47 mV dec<sup>-1</sup> (see Figure 10).

*Figure 10. Tafel plot for oxygen evolution*

The Tafel slope is an intensive parameter which does not depend on the electrode surface area so it can be used to compare the kinetics and mechanism of a reaction on different surfaces. Therefore, the observed lower Tafel slope for the Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-CoO<sub>x</sub> and Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> anodes indicates that the reaction is depolarised due to a change in the reaction mechanism rather

than a possible variation in the surface area of the anodes. Lower Tafel slopes for oxygen evolution on composite anodes containing lead and cobalt oxides have also been reported in the literature. For the evolution of oxygen from 1 mol dm<sup>-3</sup> NaOH solution, PbO<sub>2</sub>-CoO<sub>x</sub> coated anodes have shown Tafel slopes of 60-70 mV dec<sup>-1</sup>, whereas a PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> coated anode has been reported with a Tafel slope of 59 mV dec<sup>-1</sup> (Cattarin et al., 2001 and Cattarin et al., 2000). Overall, variation of the Tafel slope is a sign that the mechanism of the electrochemical reaction has changed which indicates that the electrocatalytic effect is real. In other words, significantly less energy is required to generate the same amount of oxygen gas from the sulfate electrolyte on the composite anodes developed in this study compared to the conventional PbCaSn anodes that are commonly used in industry at the moment for copper electrowinning.

#### 4 CONCLUSIONS

PbO<sub>2</sub>-based composite coatings were electrodeposited onto titanium and nickel substrates employing acetate and sulphamate solutions to prepare the composite coated anodes. Coating structures comprising both a single PbO<sub>2</sub>-based layer, and an interlayer between the substrate and the PbO<sub>2</sub>-based layer were studied, and the results showed that the layer structure has a significant influence on the behaviour of the composite coatings. Composite coated anodes consisting of a titanium substrate coated with a thermally deposited SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> interlayer followed by either an electrodeposited PbO<sub>2</sub>-CoO<sub>x</sub> or PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> surface coating were found to have the most promising stability and operating characteristics of the composite coated anodes tested in the present study, which was conducted under conditions similar to the ones used in copper electrowinning.

The Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-CoO<sub>x</sub> and Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> anodes showed different surface structure and performance. The former had a very smooth and brittle surface, while the latter anode's surface appeared very rough. Good resistance to degradation (as shown by the stability of the anode potential) was observed for the Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> coated anode over 168 hours of anodisation testing. Corrosion rate data remains to be confirmed. The electrochemical stability of the Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-CoO<sub>x</sub> anode was significantly lower under the same test conditions. The oxygen evolution reaction overpotential was just below 500 mV for both composite coated anodes in their freshly-produced state. However, this value rose to 864 mV for the Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-CoO<sub>x</sub> anode after 16 hours of anodisation testing, whereas the Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> overpotential stayed almost constant.



Corrosion tests showed a significantly lower corrosion rate for the Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-CoO<sub>x</sub> anode (1.1 g kA<sup>-1</sup> h<sup>-1</sup>) compared to the Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> anode's corrosion rate of 49 g kA<sup>-1</sup> h<sup>-1</sup>. Both corrosion rates increased when 10 mg dm<sup>-3</sup> thiourea was added to the anodisation electrolyte, to 1.3 and 79 g kA<sup>-1</sup> h<sup>-1</sup>, respectively. This is opposite to the effect of thiourea on the corrosion rate of a PbCaSn anode, where thiourea in the electrolyte reduces the corrosion rate.

The fresh Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-CoO<sub>x</sub> and Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> anodes showed Tafel slopes of 88 and 47 mV dec<sup>-1</sup> respectively. The corresponding Tafel slope of a conventional PbCaSn anode was 122 mV dec<sup>-1</sup>. The change in the Tafel slopes indicates that the evolution of oxygen on these composite anodes appears catalysed and follows a different reaction mechanism. This means that the oxygen evolution process requires significantly lower overpotential on these anodes compared to the conventional PbCaSn anodes, potentially resulting in considerable energy saving in the copper electrowinning process. In addition, the relatively slow amount of cobalt released into the electrolyte suggests that these kinds of anodes might also be suitable for use in zinc electrowinning applications.

The results from these bench scale tests demonstrate that the lead-cobalt composite coated anodes with a SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> interlayer on the surface of a titanium substrate warrant further development. The most promising composite coated anode appears to be the Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub> anode. The next challenge would be, on the one hand, to develop better understanding of the mechanism of depolarisation process, and from a practical point of view, to optimise the deposition method and produce larger scale and longer lasting composite anodes of this type.

## 5 ACKNOWLEDGMENTS

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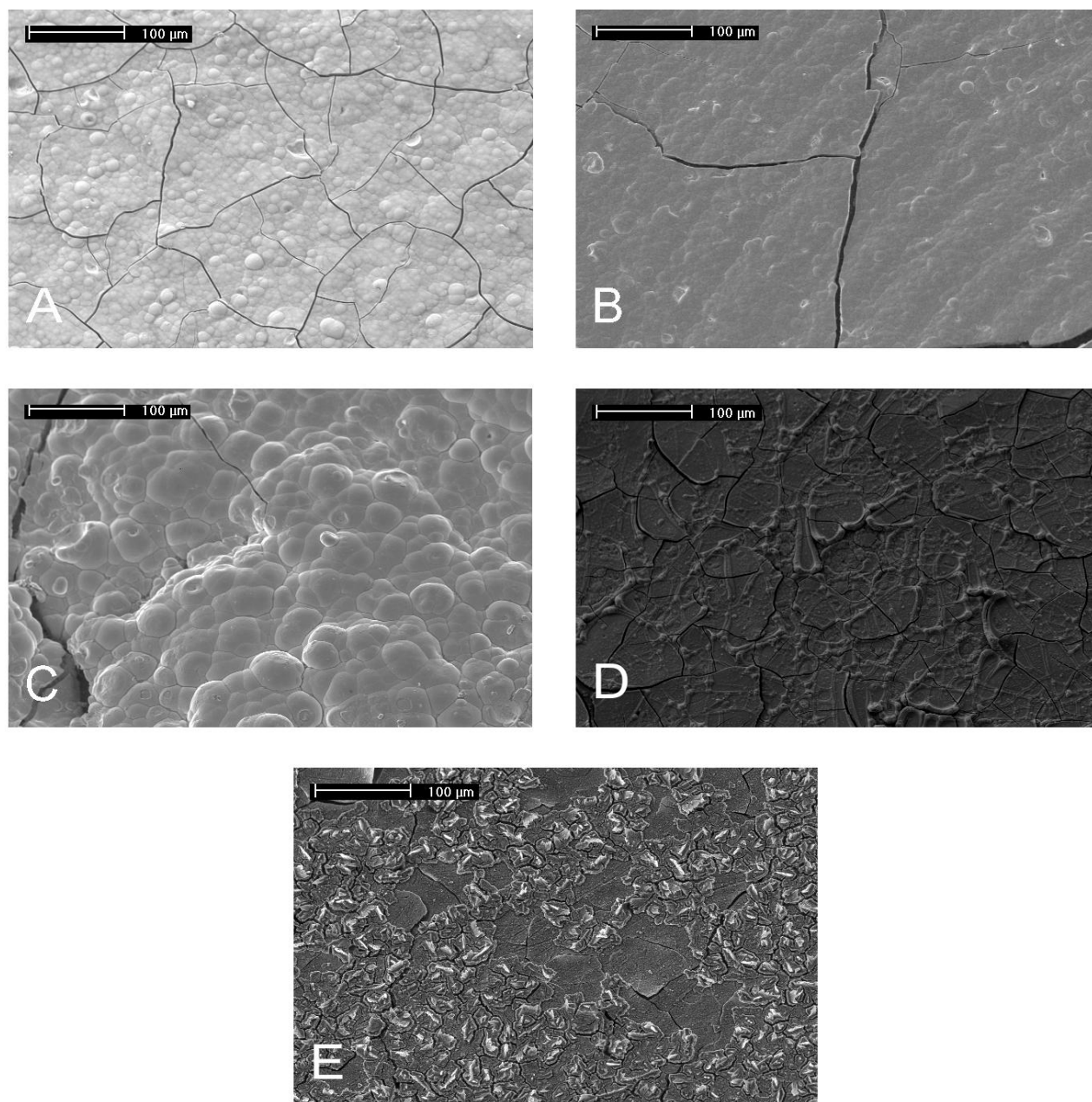


Figure 1

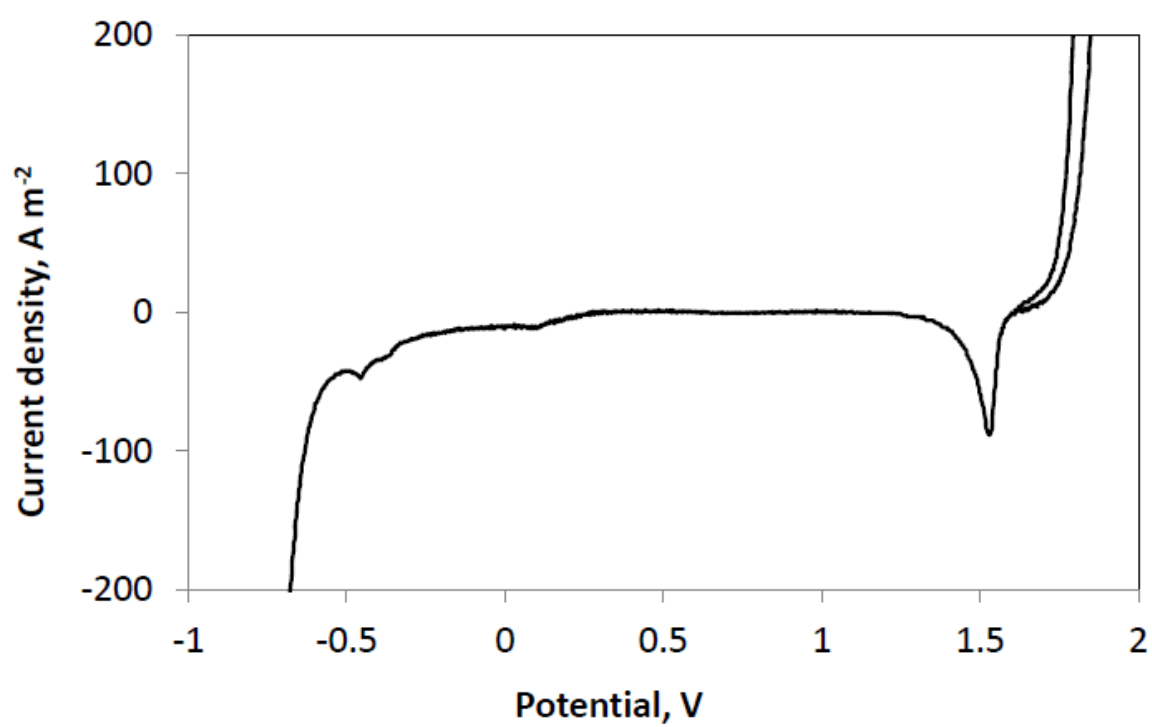


Figure 2.

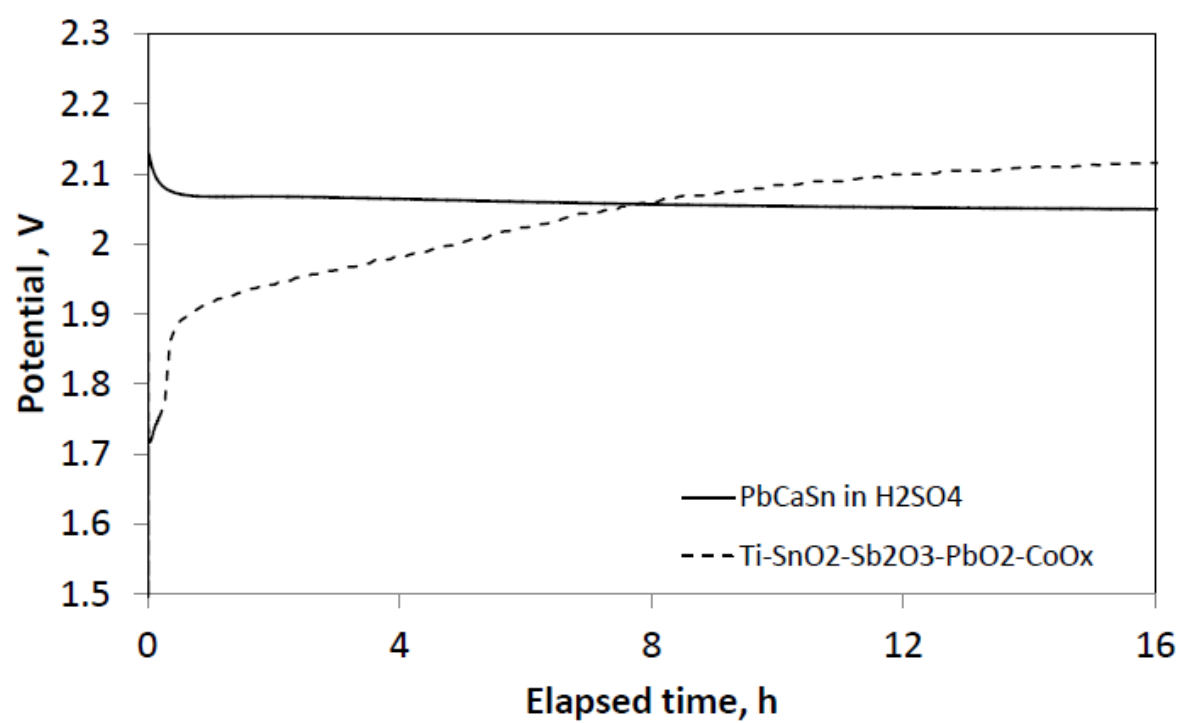


Figure 3.

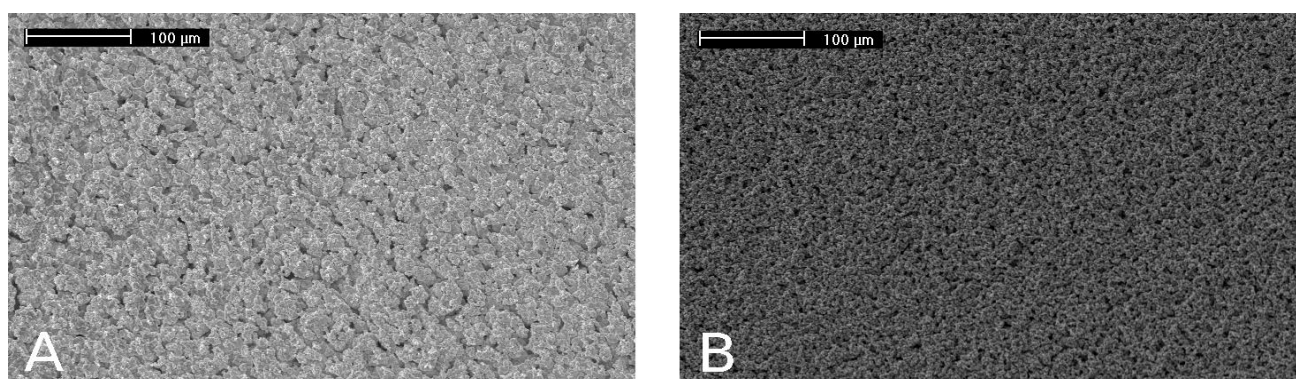


Figure 4



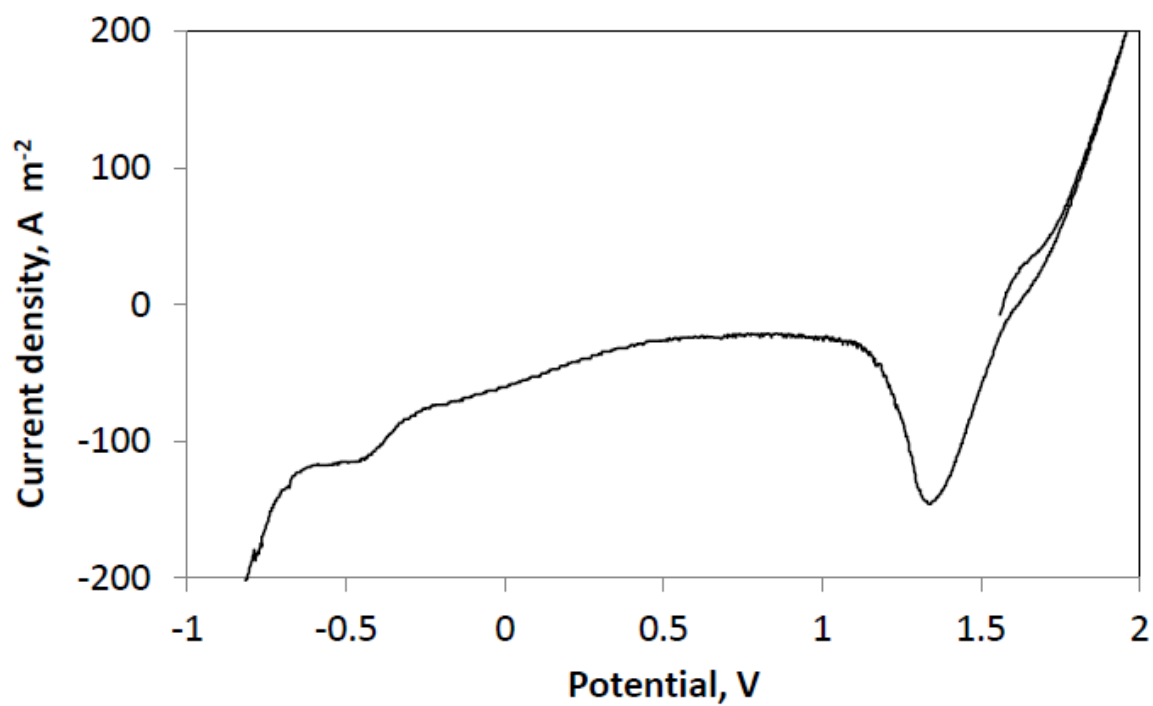


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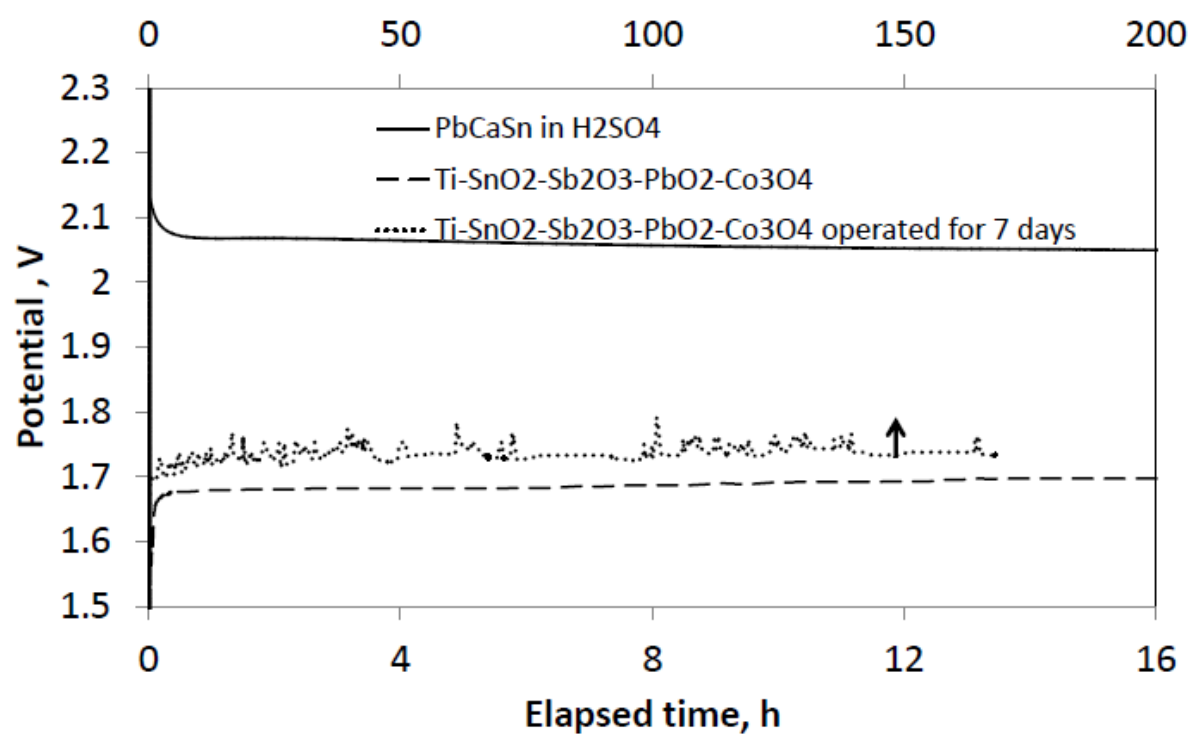


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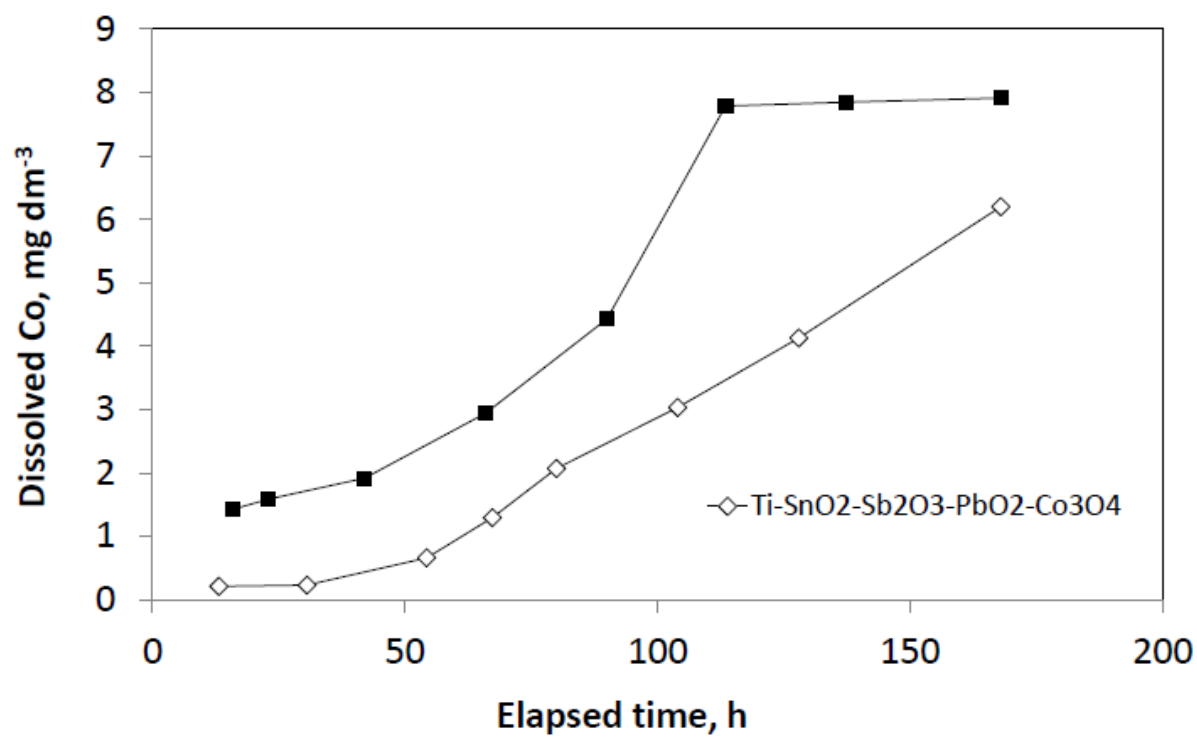


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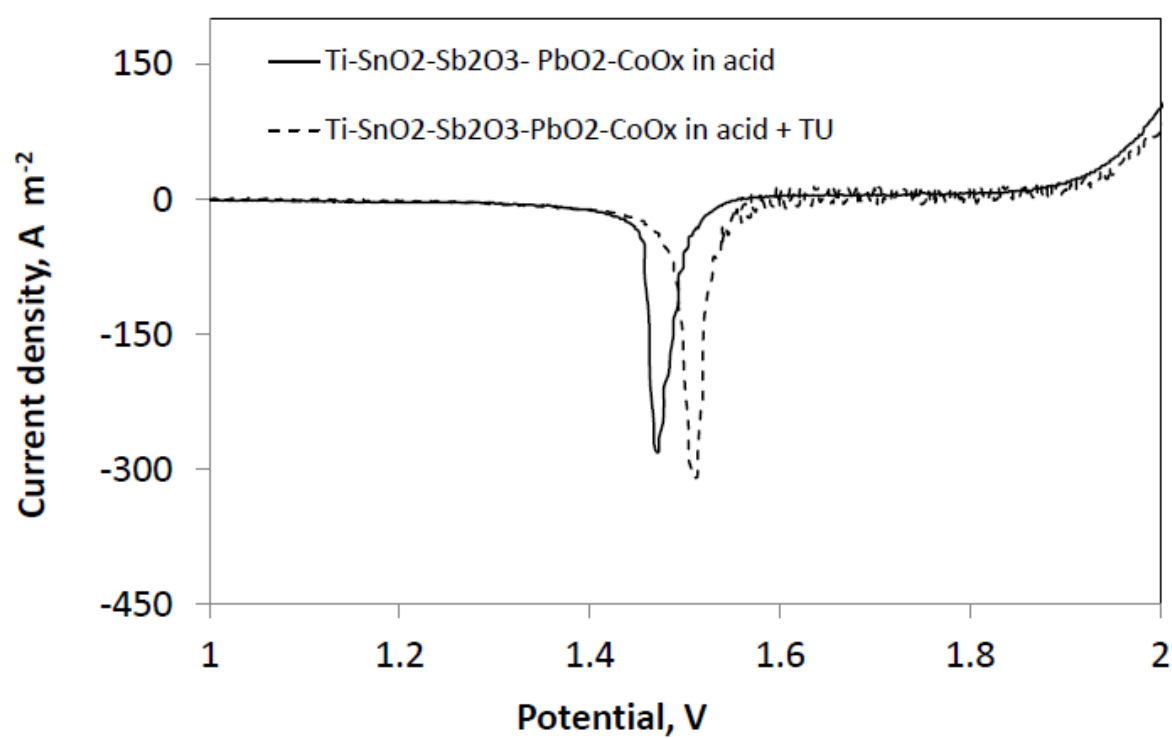


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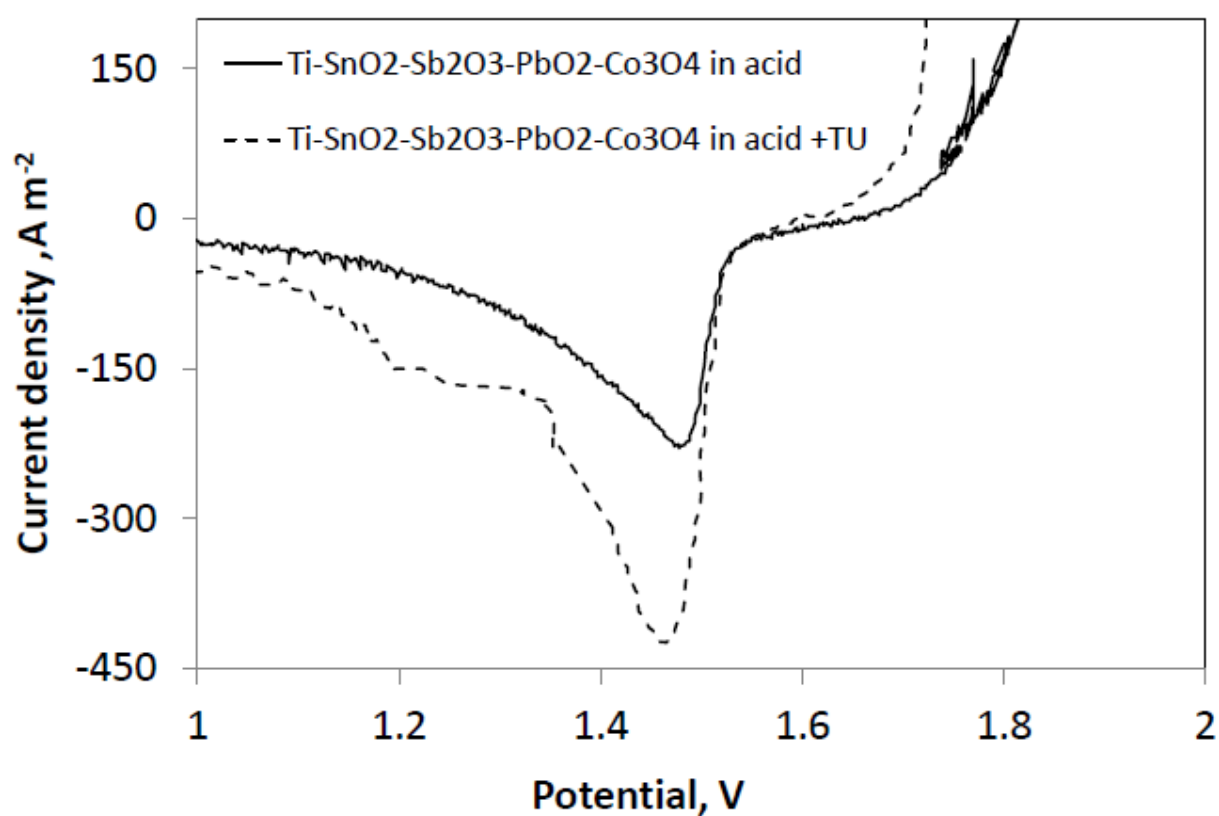


Figure 9

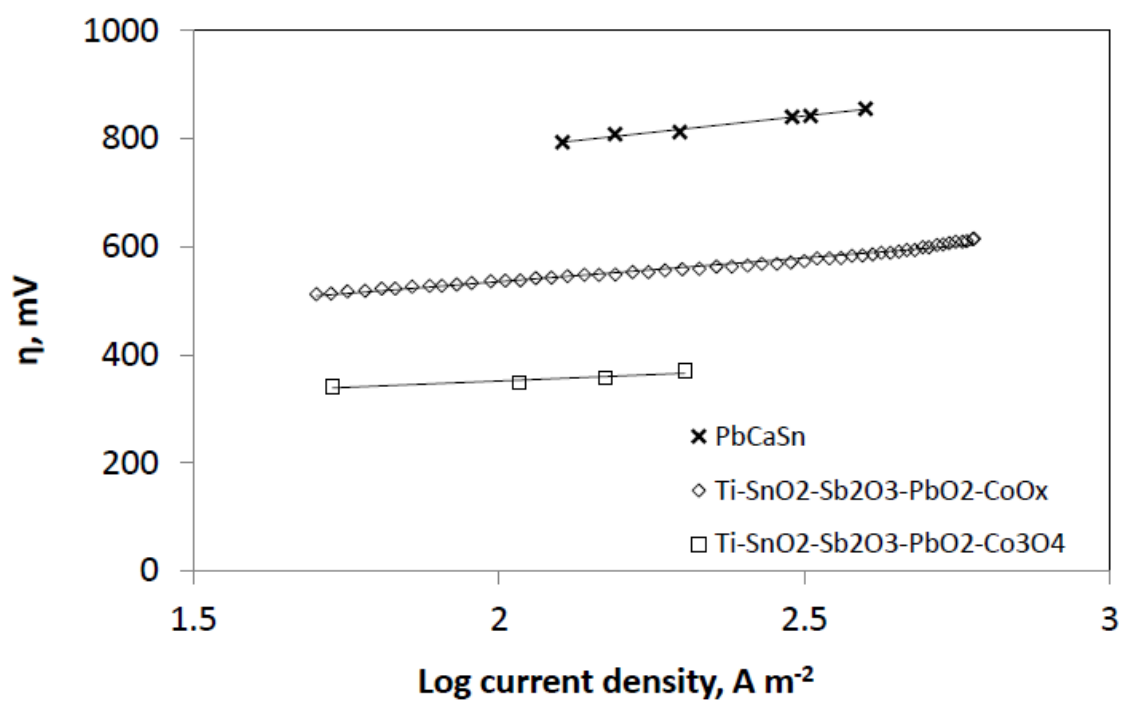


Figure 10.

*Table 1. Composition of PbO<sub>2</sub>-CoO<sub>x</sub> composite coated anodes without an interlayer and with different interlayers*

Type	Substrate	Co (at. %)	Pb (at. %)	X <sub>Co</sub> (Co/Co+Pb)
A	Ti	5.0	18.0	0.21
A	Ni	11.0	28.0	0.28
B	Ti	9.0	24.0	0.27
C	Ti	5.4	15.3	0.26
C	Ni	2.8	8.0	0.26

Table 2. Composition of  $\text{PbO}_2\text{-Co}_3\text{O}_4$  composite coated anodes without an interlayer and with different interlayers

Type	Substrate	Co (at. %)	Pb (at. %)	$X_{\text{Co}}$ (Co/Co+Pb)
A	Ti	6.0	10.0	0.60
A	Ni	17.0	11.0	0.61
C	Ti	3.2	17.0	0.16
C	Ni	20.5	7.2	0.74



Table 3. Corrosion rates of composite coated anodes and PbCaSn anode in  $180 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4$

Corrosion rate ( $\text{g kA}^{-1} \text{ h}^{-1}$ )	PbCaSn	Ti-SnO <sub>2</sub> -Sb <sub>2</sub> O <sub>3</sub> - PbO <sub>2</sub> -CoO <sub>x</sub>	Ti-SnO <sub>2</sub> -Sb <sub>2</sub> O <sub>3</sub> - PbO <sub>2</sub> -Co <sub>3</sub> O <sub>4</sub>
Without thiourea	7	1.1	49
With thiourea	4	1.3	79

Table 4. Overpotential for oxygen evolution reaction on the composite coated anodes

Composite coated anode	$\eta$ , mV (fresh anode)	$\eta$ , mV (after 16 h)	Tafel slope, mV dec <sup>-1</sup>
<b>Ti-PbO<sub>2</sub>-CoO<sub>x</sub></b>	734	-	-
<b>Ti-Pb-PbO<sub>2</sub>-CoO<sub>x</sub></b>	634	-	-
<b>Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-CoO<sub>x</sub></b>	494	864	88
<b>Ti-SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub>-PbO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub></b>	464	464	47
<b>PbCaSn</b>	834	834	122

**Highlights**

- Dimensionally stable anodes for oxygen evolution at lower overpotential than PbCaSn
- The new anodes are produced by electrodeposition of lead-cobalt composite coatings onto Ti
- Significant drop in Tafel slope suggests change in reaction mechanism for oxygen evolution
- The new anodes show promising stability operated for 7 days under copper EW conditions